



Short communication

Preparation of Au/TiO₂ by a facile method at room temperature for the CO preferential oxidation reaction

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ABSTRACT

A simple strategy was used to prepare Au/TiO₂ catalyst at room temperature. Au nanoparticles were initially prepared in solution using HAuCl₄·3H₂O as Au precursor, sodium citrate as stabilizing agent and sodium borohydride as reducing agent. The preformed Au nanoparticles were further supported on TiO₂ and the resulting solid material was characterized by Energy-dispersive X-ray spectroscopy, X-ray diffraction and Transmission Electron Microscopy and tested for the preferential oxidation of carbon monoxide in hydrogen-rich stream (CO-PROX reaction). The obtained Au/TiO₂ catalyst consisted of Au nanoparticles with an average size of ~ 4 nm and showed excellent catalytic performance in the 20–50 °C low-temperature range. In particular, at 40 °C a CO conversion of 99.5% and CO₂ selectivity of 45% were obtained using an O₂/CO ratio of 2 (1 vol% CO, λ = 4) and 97 vol% H₂ in the feed gas stream (GHSV = 15,000 mL g_{cat}⁻¹ h⁻¹).

1. Introduction

The major part of hydrogen production worldwide is originated from the combination of methane steam reforming and water-gas shift reaction chemical processes resulting in a H₂-rich gas mixture known as reformat gas, which contains 15–20 vol% CO₂, 10 vol% H₂O and ~1 vol% (10,000 ppm) of carbon monoxide (CO) [1]. The hydrogen is principally used in the ammonia synthesis for fertilizers and lately has been considered as energy carrier in a promising Polymer Electrolyte Membrane Fuel Cell (PEMFC) technology [1, 2]. However, the catalysts used in the ammonia synthesis reaction and in PEMFC devices are very sensitive to CO, and H₂ must be purified before use to reduce the CO concentration at the low ppm level (below 50 ppm) [1, 2]. The main methods employed to remove CO from the hydrogen-containing stream are pressure swing adsorption, which requires large capital investments and low flow rates, and CO methanation, the latter causing significant loss of the produced H₂ (5–15% of the generated hydrogen is consumed) due to the non-selective methanation of CO₂ present in the reformat gas [1, 2]. It was estimated that tons of annual CO₂ equivalents would be eliminated avoiding these H₂ loss [2]. The preferential

oxidation of CO with O₂ in H₂-rich mixtures (CO-PROX reaction) has been considered as a very promising alternative because it could drastically reduce the hydrogen and energy loss. It involves the oxidation of CO to CO₂ on a suitable catalyst using molecular oxygen without simultaneous oxidation of H₂ to H₂O, which would decrease the overall efficiency of the process. Thus, the main challenge is to find a suitable CO-PROX catalyst to achieve high CO₂ selectivity and high CO conversion in the presence of H₂ [2, 3].

Several studies have shown that the procedure for catalyst preparation and the nature of the oxide support play an important role for the CO-PROX reaction. Furthermore, Au nanoparticles supported on TiO₂ (Au/TiO₂ catalyst) has been considered one of the most active catalyst at low temperatures (< 100 °C). However, in order for this catalytic system to exhibit very good activities, the Au nanoparticle size should be kept below 5 nm, and this could be achieved only using suitable preparation methods [4–6].

Choudhary et al. [7] synthesized Au/TiO₂ catalysts by grafting an [Au₆(PPh₃)₆](BF₄)₂ complex onto TiO₂ and treating them thermally at different conditions prior to catalytic activity testing. At the best conditions examined, the obtained material showed a high dispersion of Au

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nanoparticles on TiO₂ and a major fraction of the Au nanoparticles were in the range of 3–6 nm (average particle size of 4.7 nm), showing a CO conversion of 32% and CO₂ selectivity of 95% at 40 °C and CO conversion of 50% and CO₂ selectivity of 73% at 80 °C. Schumacher et al. [8, 9] prepared Au/TiO₂ catalyst by a deposition-precipitation procedure, and which after treated at reducing conditions small metallic Au nanoparticles in the range of 2–3 nm were formed leading to a very active catalytic material for low-temperature CO preferential oxidation. In particular, the studies performed focused on kinetic and mechanistic aspects of the CO oxidation reaction and the influence of hydrogen on the reaction. Galletti et al. [5] prepared Au/TiO₂ catalysts by two deposition-precipitation routes and found that the catalyst prepared at lower pH values and calcined at 300 °C showed to be the most suitable for CO-PROX reaction under realistic conditions (in the presence of H₂O and CO₂). More precisely, the CO concentration was below 10 ppm within the temperature range of at least 60–80 °C, but the selectivity to CO₂ achieved was only 25%. Rossignol et al. [10] prepared Au/TiO₂ catalyst by laser vaporization of a metallic Au foil followed by deposition of the formed clusters onto the support powder, thus obtaining a narrow size distribution of highly dispersed Au nanoparticles on the support (mean particle size of 2.9 ± 1.7 nm). A CO conversion of 60% was obtained at 196 °C with CO₂ selectivity of 50%. Imai et al. [11] deposited Au nanoparticles on TiO₂ by a deposition-precipitation method, where different Au loadings (0.5–1.3 wt%) were used with nanoparticles sizes in the range of 4–6 nm. The highest CO conversion of 85% and a CO₂ selectivity of 90% were observed over the 1.3 wt% Au/TiO₂ catalyst at 22 °C.

Yang et al. [12] prepared a series of Au/TiO₂ catalysts by photo-deposition method and various preparation parameters, such as pH value, power of UV-light and irradiation were investigated. It was shown that the particle size of Au nanoparticles deposited on the support depends on the irradiation time, UV-light source and pH value of preparation solution, resulting in catalysts with narrow Au particle size distribution and particle size of ~1.5 nm. The obtained Au/TiO₂ catalysts did not require heat treatment in order to reduce the Au cations since UV-irradiation could reduce it. The catalysts were active in CO-PROX reaction and the best CO conversion and CO₂ selectivity found were 95% and 47%, respectively, at 80 °C. Yu et al. [13] prepared Au/TiO₂ via deposition-precipitation method and observed that the pH adjustment time for gold colloid solution was relevant to the performance of the catalyst resulting in catalyst with good activity between 25 and 50 °C. Chang et al. [14] also prepared Au/TiO₂ catalysts by deposition-precipitation method and observed maximum CO conversion at 100 °C. Mahmood and Woo [15] described an enhancement in the catalytic activity of Au/TiO₂ prepared by deposition-precipitation method for the CO-PROX reaction due to the formation of active Au metal sites on the catalyst surface by the thermal treatment applied, where small gold nanoparticles were formed after plasma treatment. In fact, following thermal and plasma treatment the Au/TiO₂ catalysts showed better activity than the untreated Au/TiO₂ catalysts and a CO conversion of 75% and CO₂ selectivity of 30% at 100 °C were obtained.

In this work, a simple synthetic strategy was used to prepare a Au/TiO₂ catalyst, where Au nanoparticles were first prepared in solution using citrate as a stabilizing agent, and sodium borohydride as reducing agent. The pre-formed Au nanoparticles were then deposited onto the TiO₂ carrier and the resulting Au/TiO₂ solid showed excellent catalytic performance for the CO-PROX reaction at low temperatures (20–50 °C).

2. Experimental

2.1. Preparation of Au/TiO₂ catalysts

Firstly, Au nanoparticles were prepared using HAuCl₄·3H₂O as Au precursor, sodium citrate as stabilizing agent and sodium borohydride as reducing agent. An aqueous solution of the Au precursor (3.95 × 10⁻⁴ mol L⁻¹) and sodium citrate (1.186 × 10⁻³ mol L⁻¹) in a

molar ratio of citrate:Au of 3 were first mixed, and a solution of sodium borohydride (2.391 × 10⁻³ mol L⁻¹) (BH₄⁻:Au molar ratio of 6) was then added under magnetic stirring at room temperature. Immediately, a red color solution was formed. In a subsequent step, the TiO₂ support (Degussa P25) was added to this solution and the resulting mixture was kept under stirring for 24 h. After this period, the solid material (Au/TiO₂) was separated by centrifugation, washed with water and dried at 80 °C for 2 h.

2.2. Catalysts characterization

The chemical composition of the catalysts was determined using a Philips Scanning Microscope (model XL30 with electron beam of 20 keV) equipped with EDAX microanalyzer (model DX-4). Data were collected at 4 random points of the sample and the final result corresponds to the average of these points.

Powder X-ray diffractograms were obtained in a Rigaku diffractometer (model Miniflex II, Cu K α radiation source ($\lambda = 1.54 \text{ \AA}$)), with scanning at 2θ from 20 to 90° with 0.05 step and 2 s count.

The Au particle size distribution was examined in a Transmission Electron Microscope (TEM) (model JEM-2100 and TEM-FEG JEM-2100F, 200 kV). For the analysis, a suspension of each catalyst in 2-propanol was prepared, where it was homogenized in an ultrasonic system. Subsequently, an aliquot of the sample was deposited on a copper grid (0.3 cm in diameter) with a carbon film. Eight micrographs on average were taken, so the data collection allowed the construction of a histogram that represented the size distribution of the Au nanoparticles.

2.3. Catalytic performance

The as-prepared Au/TiO₂ catalyst was evaluated in a fixed bed reactor in the temperature range of 25–120 °C. The inlet gas was fed at the flow rate of 25 mL min⁻¹ with the following composition (vol%): 1% CO, 2% O₂ and 97% H₂. The mass of the catalyst in the catalytic bed was 100 mg (space velocity = 15,000 mL g_{cat}⁻¹ h⁻¹). No catalyst pre-treatment was applied before catalyst testing. The reaction product stream was analyzed by gas chromatography (GC) and quantified using calibration curves. The CO conversion, O₂ consumed and CO₂ selectivity were calculated according to the following Eqs. (1)–(2):

$$\text{CO conversion} = 100 \times ([\text{CO}]_{\text{in}} - [\text{CO}]_{\text{out}}) / [\text{CO}]_{\text{in}} \quad (1)$$

$$\text{CO}_2 \text{ selectivity} = 100 \times (0.5 \times [\text{CO}_2]_{\text{out}}) / ([\text{O}_2]_{\text{in}} - [\text{O}_2]_{\text{out}}) \quad (2)$$

3. Results and discussion

The Au nanoparticles were prepared in solution using sodium citrate as stabilizing agent and sodium borohydride as reducing agent. The Au precursor and sodium citrate were dissolved in water and after the borohydride solution was added to this solution at room temperature, a clear red solution was formed. The methodology used to prepare Au nanoparticles was similar to the one described by Jana et al. [16] except that the latter added ice-cold borohydride to the solution. The transmission electron micrograph of this solution showed the presence of Au nanoparticles with particles sizes in the range of 3–5 nm and an average particle size of ~4 nm (Fig. 1a). It is noteworthy that Au nanoparticles solution prepared in this way remains stable for several weeks. In a subsequent step, an appropriate amount of TiO₂ support was added to the Au nanoparticles solution in order to obtain Au/TiO₂ catalyst with 1 wt% loading of Au. The EDX analysis of the resulting Au/TiO₂ catalyst showed that the contents of Au (1.02 wt%) and TiO₂ (98.98 wt%) were very similar to the nominal values, indicating that all Au nanoparticles were deposited on the TiO₂ support. The transmission electron micrographs of Au/TiO₂ catalyst (Fig. 1b) show a good distribution of Au nanoparticles on the TiO₂ support with an average size of ~4 nm

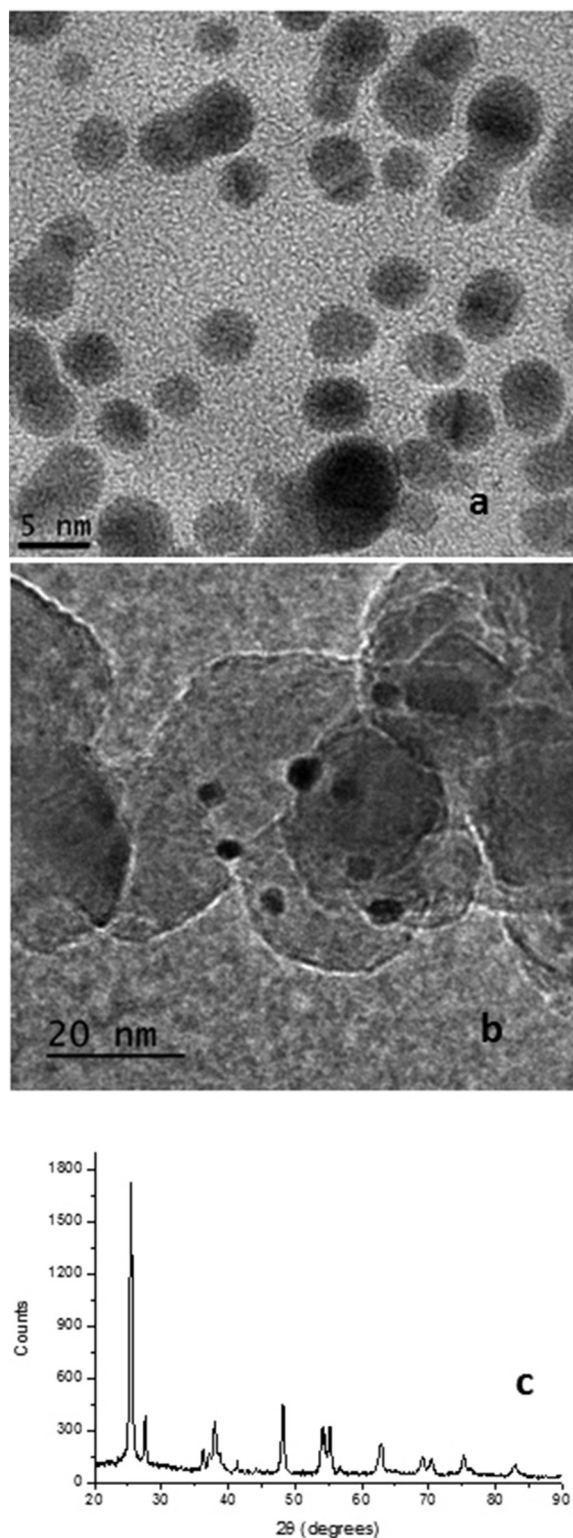


Fig. 1. TEM micrographs of the pre-formed Au nanoparticles (a) and those supported on TiO₂ (b), and X-ray diffractogram of the Au/TiO₂ catalyst (c).

showing that Au nanoparticles were not altered. It can be emphasized that Au/TiO₂ catalysts with different Au contents (wt%) but similar nanoparticles sizes could be prepared after using this methodology.

The X-ray diffractogram of Au/TiO₂ (Fig. 1c) shows only the well-defined and high intensity crystalline peaks of anatase ($2\theta = 25.3^\circ$, 37.7° , 47.9° , 53.8° and 62.5°) and rutile (at $2\theta = 27.4^\circ$, 36.1° and 54.4°)

crystal phases [12, 17] present in the TiO₂ support (P25 Degussa); however, the peaks of face-centered cubic (fcc) phase of Au nanoparticles at $2\theta = 38.2^\circ$, 44.5° , 64.5° , 77.5° and 81.7° [10] were not observed in the diffractograms due its small size, resulting in broad and low-intensity peaks that were too small to be clearly detected by XRD [12].

The catalytic performance of Au/TiO₂ is shown in Fig. 2a. No previous treatments were done in this sample and the results shown correspond to the first cycle of the catalytic reaction. An increase of CO conversion with increasing temperature is observed reaching values of ~90% at 120 °C. On the other hand, the CO₂ selectivity values obtained are very low reaching a maximum value of 20% at 120 °C. The O₂ consumption increases sharply above 60 °C, which signifies the fact that the undesired reaction of hydrogen oxidation to water is favored.

In the second catalytic cycle, a large increase in CO conversion and CO₂ selectivity already occurs at low temperatures (Fig. 2 b). This significant improvement of catalytic activity may be attributed to a decrease in the amount of Au cationic species due their reduction by hydrogen and/or CO in the first catalytic cycle. Schumacher et al. [8] described a significant increase of activity upon reductive activation of Au/TiO₂ catalyst and suggested that small metallic Au particles and not ionic Au species should be considered as the most active species for CO oxidation. Other possibilities could be the degradation of the citrate shell, which may lead to a better accessibility of the Au surface and/or modifications on Au nanoparticles morphology or Au-support interactions under reaction conditions [18].

In the second cycle at 20 °C, a CO conversion of 75% and a CO₂ selectivity of ~45% are obtained. By increasing the reaction temperature to 45 °C a CO conversion of 99% and a CO₂ selectivity of 40% are obtained. A typical goal for CO-PROX reaction, which arises from the requirements for PEMFC is to reduce the CO concentration of the hydrogen-rich mixtures to 50 ppm with a CO₂ selectivity $\geq 50\%$, defined as the goal 50/50 [2]. Also, the total CO conversion at ambient temperatures is particularly important for PEMFC applications in transportation [19]. In the second cycle, when the reaction temperature was increased above 45 °C, the CO conversion and CO₂ selectivity decrease sharply, favoring the undesired reaction of hydrogen oxidation. This catalytic activity profile was also reported for other Au/TiO₂ catalysts prepared by different methodologies [5–7, 10–15]. More precisely, the CO conversion does not present a monotonous behavior with increasing temperature; it increases with temperature until the highest conversion is achieved, and then decreases because oxygen is preferentially participating in the undesired H₂ oxidation reaction, whereas the CO₂ selectivity is high at low temperatures and decreases steadily with increasing temperature.

Comparing the present results with those reported in the open literature (Table 1), it could be seen that only few Au/TiO₂ catalysts [11, 13] present similar performance at low temperatures (20–50 °C), while most of them perform reasonably well only at temperatures equal or > 80 °C. Imai et al. [11] reported on the Au/TiO₂ catalyst prepared by the deposition-precipitation method and calcined at 250 °C before reaction, a CO conversion of 85% and a CO₂ selectivity of 90% at 22 °C. However, by increasing the reaction temperature to 45 °C the CO conversion decreased to around 70% and the CO₂ selectivity to 60%. These results were obtained using a similar space velocity and H₂ concentration in the inlet gas stream but with a lower O₂/CO ratio of 0.5 ($\lambda = 1$) when compared to the present results. Yu et al. [13] reported for a Au/TiO₂ catalyst prepared by the deposition-precipitation method a CO conversion of 99% and a CO₂ selectivity of 50% in the range of 25–50 °C using a lower H₂ feed concentration (50 vol%) and O₂/CO ratio of 1 ($\lambda = 2$) but with a larger space velocity. It should be emphasized at this point that in the present catalytic experiments a volumetric O₂/CO ratio of 2 ($\lambda = 4$) was used, that is, a reasonable excess of oxygen, whereas an O₂/CO ratio of 0.5 and 1.0 ($\lambda = 1$ and 2) was commonly used [6, 10–14] (see Table 1). It has been reported that lower λ values resulted

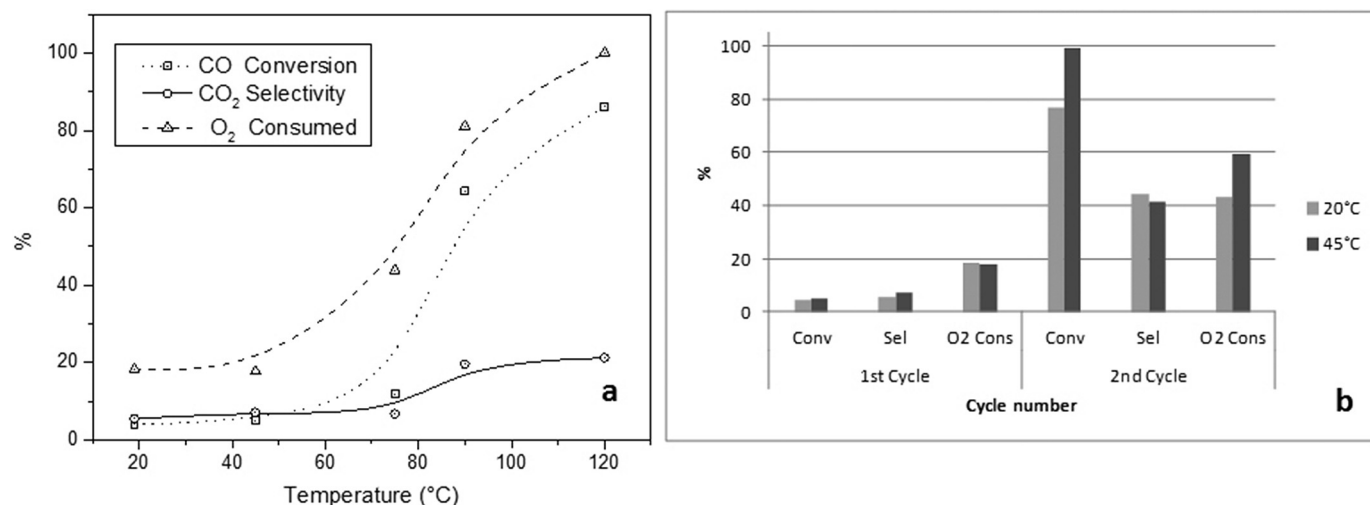


Fig. 2. CO conversion (%) and CO₂ selectivity (%) as a function of reaction temperature - first cycle (a), and comparison of the catalytic performance results of the first and second cycles (b).

in higher selectivity values for the CO-PROX reaction [20], thus, even if a high value of λ were to be used in our catalytic experiments, a good CO₂ selectivity could be obtained. In addition, a higher concentration of H₂ was also used (97 vol%) in the present CO-PROX catalytic experiments, whereas typically a concentration of approximately 50 vol% was reported [5–7, 10, 12–15].

The long-term test results for the Au/TiO₂ catalyst at 45 °C are shown in Fig. 3. The CO conversion reached 99.5% and the CO₂ selectivity was maintained at ~45% showing that the catalyst remained stable throughout the period evaluated even using a volumetric O₂/CO ratio of 2 ($\lambda = 4$) and 97 vol% of hydrogen in the feed gas stream. If lower λ values and hydrogen concentrations would be used, the CO₂ selectivity values could likely be further improved.

4. Conclusions

A Au/TiO₂ catalyst with Au metal average nanoparticles size of ~ 4 nm could be prepared by a facile method at room temperature. The catalyst showed to be very active, selective and stable (18 h on reaction stream) for the CO-PROX reaction at low temperatures (20–50 °C), even at a high volumetric O₂/CO ratio and high hydrogen concentration in the inlet feed gas stream. The influence of synthesis parameters, like citrate: Au and BH₄⁻: Au molar ratios on Au nanoparticles size and the influence of reaction parameters on the CO conversion and CO₂ selectivity, like a volumetric O₂/CO ratio, space velocity, hydrogen concentration and the presence of H₂O and/or CO₂ in the inlet feed gas stream are under investigation.

Table 1

Comparison of the catalytic performance over Au/TiO₂ catalysts for CO-PROX reaction reported in the literature.

Method	Catalyst treatment process before reaction	Au metal loading (wt %)	Au particle size (nm)	Feed composition (vol%)	O ₂ /CO feed ratio	Space velocity	T (°C) ^a	CO conversion (%)	CO ₂ selectivity (%)	Reference
Deposition Precipitation	Calcined at 300 °C	2	–	CO/O ₂ /H ₂ /CO ₂ /H ₂ O/He 1/2/37/18/5/37	2	40.000 mL g ⁻¹ h ⁻¹	60–80	99.99	20	[5]
Direct anionic exchange (DAE)	Ammonia treatment	1.5	3	CO/O ₂ /H ₂ /He 2/2/48/48	1	3.000 h ⁻¹	100	88	45	[6]
Impregnation Au complex	Heating H ₂ at 500 °C and calcined at 400 °C	1	4.7	CO/O ₂ /H ₂ /He 1/2/50/25	2	90.000 mL g ⁻¹ h ⁻¹	100	55	30	[7]
laser vaporization of a metallic gold	No treatment	0.023	2.9	CO/O ₂ /H ₂ /He 2/2/48/48	1	4.000 mL g ⁻¹ h ⁻¹	200	60	40	[10]
Deposition Precipitation	Calcined at 250 °C	1.3	5.7	CO/O ₂ /H ₂ 1/0.5/98.5	1	20.000 mL g ⁻¹ h ⁻¹	22	85	90	[11]
Photo-deposition	No treatment	1	~1.5	CO/O ₂ /H ₂ /He 1.33/1.33/65.33/32.01	1	30.000 mL g ⁻¹ h ⁻¹	80	95	47	[12]
Deposition Precipitation	No treatment	3	≥ 5 nm	CO/O ₂ /H ₂ /N ₂ 1/1/50/48	1	165.000 mL g ⁻¹ h ⁻¹	25–50	99	50	[13]
Deposition Precipitation	Calcined at < 200 °C	0.5	2.5	CO/O ₂ /H ₂ /He 1.33/1.33/65.33/32.01	1	30.000 mL g ⁻¹ h ⁻¹	80	70	35	[14]
Deposition Precipitation	Thermal and Plasma Treatment	1.0	2.8	CO/O ₂ /H ₂ /N ₂ 1/1/50/48	2	120.000 h ⁻¹	100	75	30	[15]
Supported pre-formed Au nanoparticles	No treatment	1.0	4	CO/O ₂ /H ₂ 1/2/97	2	15.000 mL g ⁻¹ h ⁻¹	45	99	45	This work

^a Temperature of maximum CO conversion.

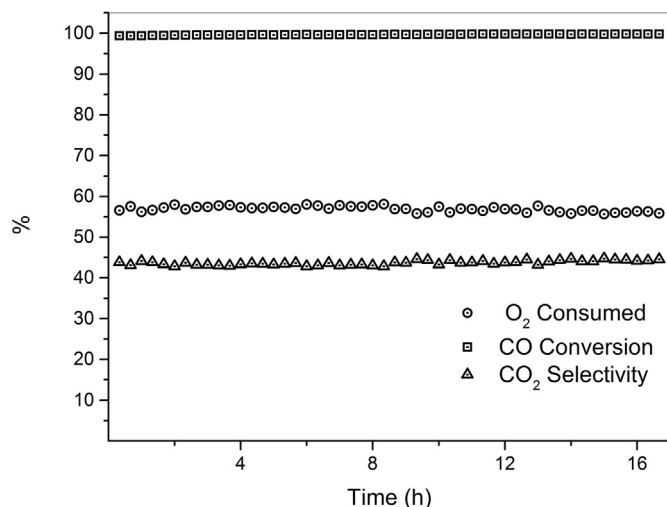


Fig. 3. CO conversion (%) and CO₂ selectivity (%) at 45 °C vs. time on stream – stability test.

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